



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

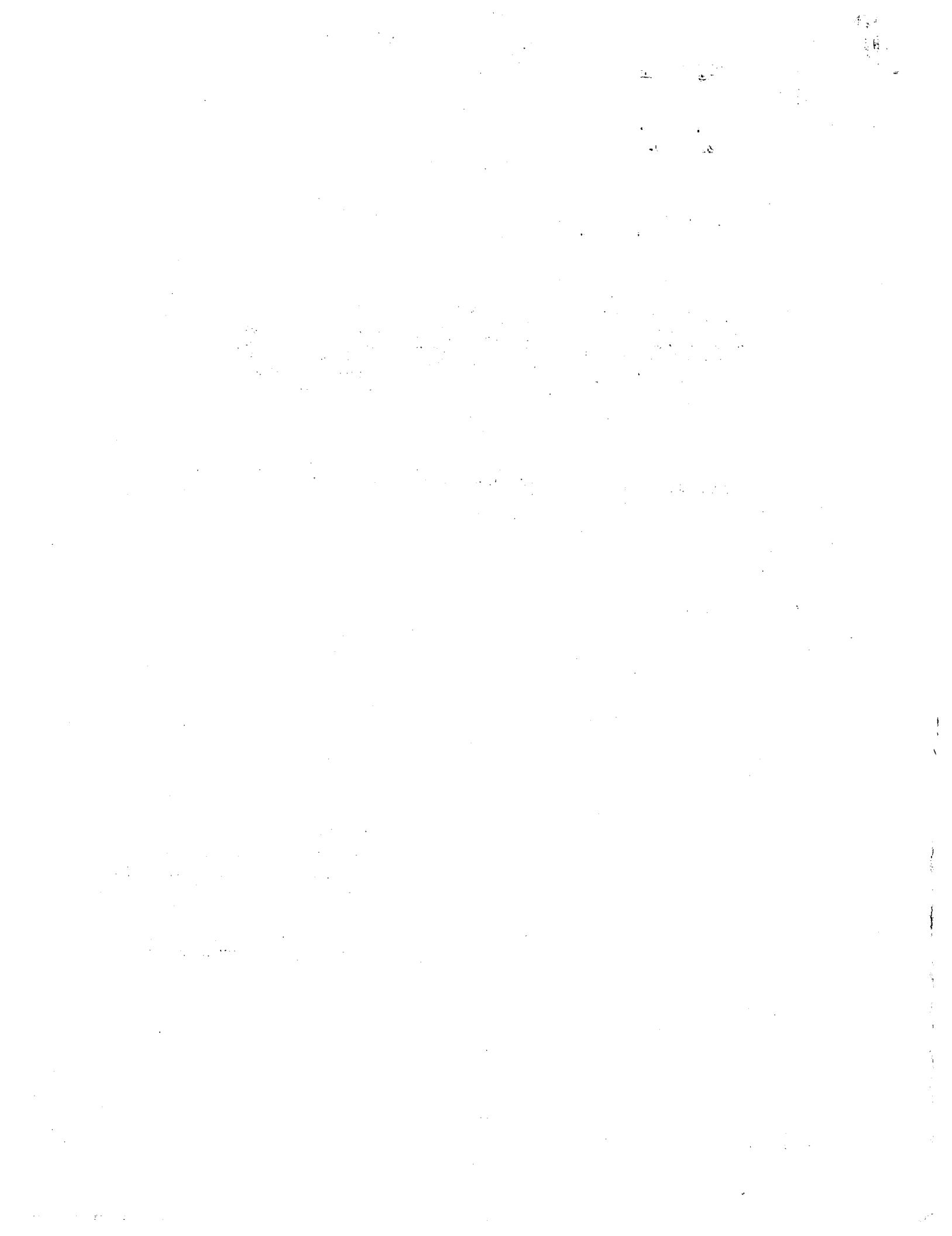
02102090.4

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk





Anmeldung Nr:
Application no.: 02102090.4
Demande no:

Anmeldetag:
Date of filing: 02.08.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

AGFA-GEVAERT
Septestraat 27
2640 Mortsel
BELGIQUE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Stimulable phosphor screen showing less scattering upon stimulation

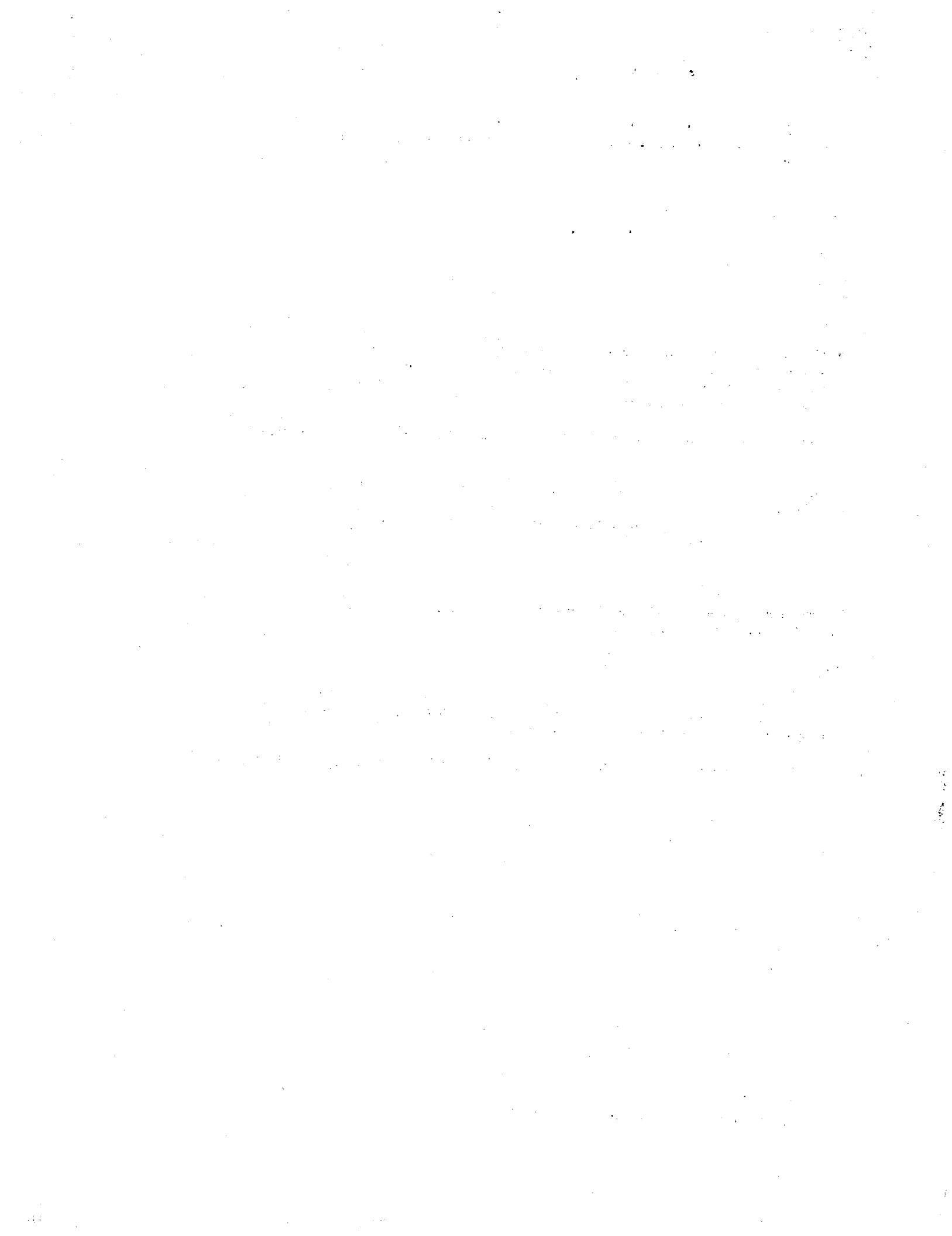
In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

G21K/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignés lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR



- 1 -

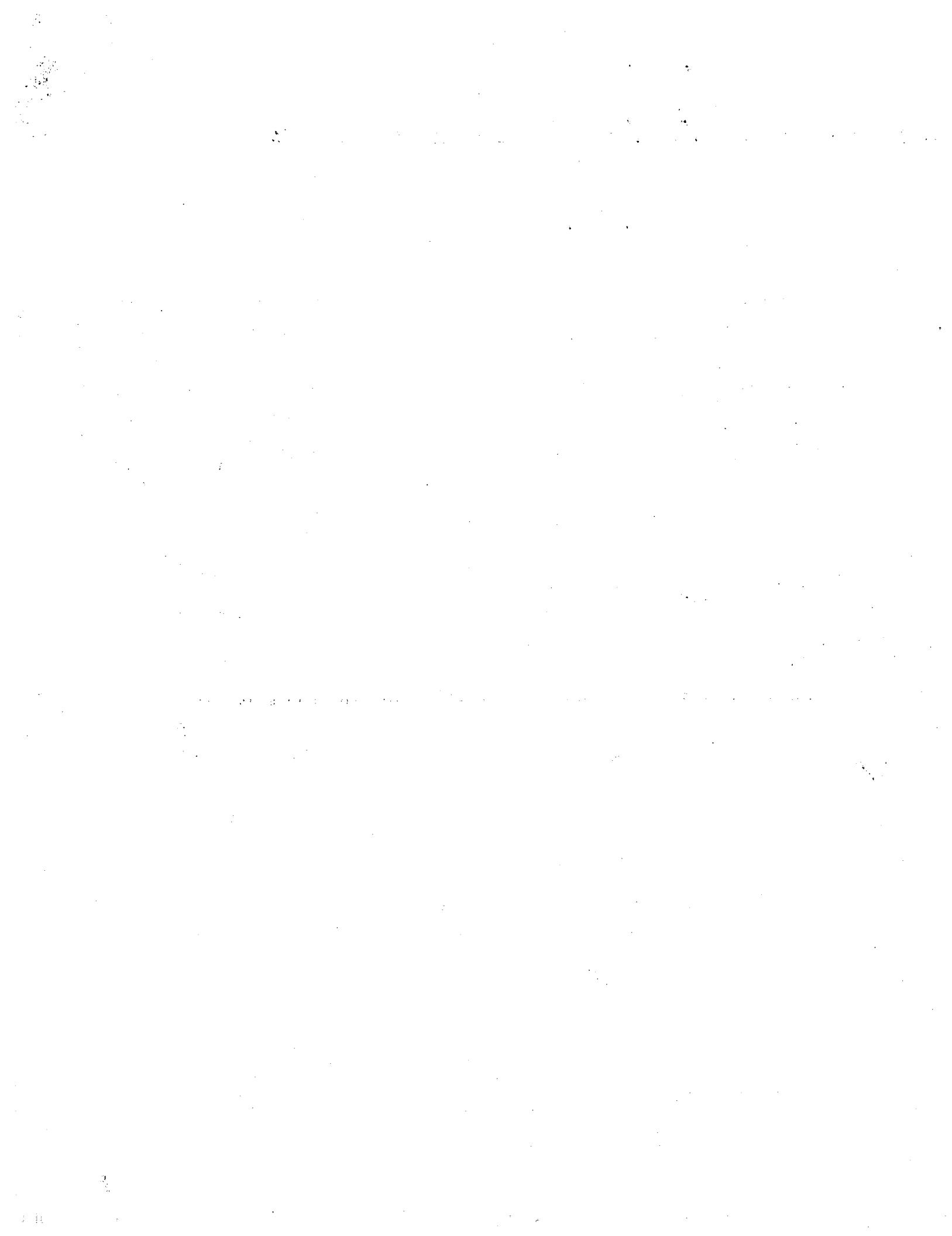
[ABSTRACT]

TITLE

5 STIMULABLE PHOSPHOR SCREEN SHOWING LESS SCATTERING UPON STIMULATION

A stimulable phosphor screen or panel has been described, said screen comprising a support, a layer of lead or a layer containing a lead compound, and a storage phosphor layer, wherein the layer containing lead or a lead compound is present as an intermediate layer between said support and said storage phosphor layer.

15



- 2 -

[DESCRIPTION]

FIELD OF THE INVENTION

5 The present invention relates to a method for storing and
reproducing a radiation image, making use of a radiation image
storage sheet or panel and to a radiation image storage screen or
panel with a stimulable phosphor layer and a layer arrangement
suitable for use in the said radiation image storing and reproducing
10 method.

BACKGROUND OF THE INVENTION

15 As a method replacing conventional radiography, radiation image
storing and reproducing methods have been proposed, making use of an
image storage screen or panel, known as comprising a sheet or layer
comprising a stimulable phosphor. The method thereby comprises the
steps of causing the stimulable phosphor of the storage panel to
20 absorb radiation energy having passed through an object or having
radiated from an object; sequentially exciting the stimulable
phosphor with an electromagnetic wave such as visible light or
infrared rays (i.e., stimulating light) in order to release the
radiation energy stored in the phosphor as light emission (i.e.,
25 stimulated emission); photoelectrically detecting the emitted light
to obtain electric signals; and reproducing the radiation image of
the object as a visible image from the electric signals. In order
to be repeatedly employed the panel is further subjected to a step
for erasing radiation energy remaining therein, and then stored for
30 the next image storing and reproducing procedure.

So in US-A 3,859,527 e.g. a method for producing X-ray images with a photostimulable phosphor, which are incorporated in a panel, is disclosed. The panel is exposed to incident pattern-wise modulated X-ray beam and as a result thereof the phosphor temporarily stores energy contained in the X-ray radiation pattern.

At some interval after the exposure, a beam of visible or infra-red light scans the panel in order to stimulate the release of stored energy as light that is detected and converted to sequential electrical signals which are processed in order to produce a visible image. For this purpose the phosphor should store as much as possible of the incident X-ray energy and emit as little as possible of the stored energy until stimulated by the scanning beam. This is called "digital radiography" or "computed radiography".

In applications for digital radiography image quality is very important. A high image definition and a low noise level is highly desired. Image definition (sharpness) is, to a large extent, defined by scattering properties of the phosphor layer. As a consequence thereof phosphor layer thickness is limited by the desired sharpness. More particularly in mammographic applications sharpness should be extremely high in order to have an image having high enough a diagnostic value, without leaving any doubt with respect to presence or absence of microcalcifications, in order to furthermore avoid retakes. Phosphor layer thicknesses should therefore not exceed 150 μm in order to get the desired sharpness or image definition. In praxis however it has been established that image definition does not reach the expected level and that although all measures have been taken in order to reach it, an unexpectedly lower level is attained.

The image quality that is produced by any radiographic system using a phosphor screen, thus also by a digital radiographic system, largely depends on the construction or layer arrangement of the phosphor screen. In general the thinner a phosphor screen at a given amount of absorption of X-rays, the better the image quality will be. This means that the lower the ratio of binder to phosphor of a phosphor screen, the better the image quality, attainable with that screen, will be. Optimum sharpness can thus be obtained when screens without any binder are used. Such screens can be produced e.g. by physical vapour deposition, which may be thermal vapour deposition, sputtering, electron beam deposition or other of

- 4 -

phosphor material on a substrate. However, this production method can not be used in order to produce high quality screens with every arbitrary phosphor available. The mentioned production method leads to the best results when phosphor crystals with high crystal symmetry and simple chemical composition are used.

The use of alkali metal halide phosphors in storage screens or panels is well known in the art of storage phosphor radiology and the high crystal symmetry of these phosphors makes it possible to simultaneously provide structured screens and binderless screens.

It has been disclosed that when binderless screens with an alkali halide phosphors are produced it is beneficial to have the phosphor crystal deposited as some kind of piles, needles, tiles, etc.. In US-A-4 769 549 it has been disclosed that the image quality of a binderless phosphor screen can be improved when the phosphor layer has a block structure shaped in fine pillars. In US-A 5,055,681 a storage phosphor screen comprising an alkali halide phosphor in a pile-like structure has been disclosed. The image quality of such screens needs still to be increased and in JP-A-06/230 198 it is disclosed that the surface of the screen with pillar like phosphors is rough and that a levelling of that surface can increase its sharpness. In US-A 5,874,744 attention is drawn to the index of refractivity of the phosphor used to produce the storage phosphor screen with needle-like or pillar-like phosphors.

In EP-A 1,113,458 a binderless storage phosphor screen has been disclosed that comprises an alkali metal storage phosphor characterised in that said screen shows an XRD-spectrum with a (100) diffraction line having an intensity I_{100} and a (110) diffraction line having an intensity I_{110} , so that $I_{100}/I_{110} \geq 1$. Such a phosphor screen shows a better compromise between speed and sharpness.

Although all screens disclosed in this prior art can yield X-ray images with good quality, the need for a better compromise between speed of the recording system (i.e. as low as possible a patient dose) and an image with high sharpness and low noise is still there.

5

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide a
10 stimulable phosphor screen useful in an X-ray recording system with an excellent compromise between speed of the recording system (i.e. as low as possible patient dose) and an image with high sharpness and low noise as normally expected.

The above mentioned object has been realised by providing a
15 stimulable phosphor screen having the specific features defined in claim 1. Specific features for preferred embodiments of the invention are disclosed in the dependent claims.

Further advantages and embodiments of the present invention will become apparent from the following description and drawings.

20

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a storage phosphor panel having a lead foil as an
25 intermediate layer between support (PET, Al, Glass, Amorphous Carbon) and phosphor layer, coated with a stimulable phosphor (BaFBr:Eu, CsBr:Eu)

Fig. 2 shows a panel having a layer of lead glass between a
30 conventional phosphor layer (with CsI:Eu as conventional phosphor) and an electronic detector (CCD, Diode array).

35

- 6 -

DETAILED DESCRIPTION OF THE INVENTION

It has been found that, to an unexpected extent, sharpness is not only determined by the scattered radiation passing the phosphor layer and depending on the content and thickness of that layer, but to an even more important extent to scattering of radiation once impinging upon and passing the support layer or undercoat layer, which may be the same or different.

Whereas in the storage phosphor layer scattering properties are normally related with radiation in the wavelenght range of visible stimulated light, the support or undercoat layer may cause scattering of X-rays, effecting the said support or undercoat layer, a phenomenon also known as "backscattering".

The said "backscattering" is generated in all layers, known as supporting or undercoating, wherein said undercoating layers may be between the supporting and the phosphor layers as intermediate layers.

These considerations having been taken in mind and moreover having the knowledge that the undercoat layer or support is not strongly absorbing X-rays, it is clear that X-rays are penetrating to a remarkable depth into the layers under the phosphor layer(s), and that "backscattering" appears in all layers farther from the radiation source than the phosphor layer. So to say: "backscattering" provokes "exposure of more than one pixel" and lays burden on the expected sharpness as really attained. As a result loss in sharpness is found to occur.

Following solutions have been found in order to get rid of the "backscattering loss factor" described above.

In one embodiment according to the present invention it has been established that a thin intermediate layer of a material strongly absorbing X-rays, wherein said material layer is present between

phosphor layer and underlying support layer, provides a substantially improved sharpness. This result can be interpreted to be due to the smaller distance over which "backscattering" is set free in order to effect "neighbouring pixels". As a strongly absorbing material for the said intermediate layer lead or a lead compound is highly preferred.

In another embodiment according to the present invention it has been established that it is sufficient to have a material in the intermediate layer as set forth above, wherein the said material may be absorbing X-rays to a lower extent, but wherein it nevertheless avoids scattering to a great extent. As a consequence presence of less scattered light is not related with a real "depth" where scattered radiation is generated as no more than one pixel is overlapped by said "scattering".

From lead as a preferred metallic material it is also known that, from the point of view as set forth in the second embodiment, that the amount of generated "backscattering radiation" in a layer of lead is much lower than in a layer of e.g. aluminum or tungsten. A preferred alternative for supporting the preferred lead metal, is amorphous carbon(a-C), not only thanks to the black, radiation absorbing particles, but, to a more remarkable extent, thanks to the generation of very little backscattering.

As a result presence of a thin intermediate layer comprising lead or a lead compound supported by amorphous carbon is highly recommended. Although it is known in the art that a "thick" layer, foil or screen of lead may be present in a cassette wherein a phosphor plate is used, said foil or screen is known to have been situated at a distance far from the phosphor layer and not as a coated layer between said phosphor layer and the support layer of the said phosphor layer. It was moreover found now that including an amorphous carbon film as support did open perspectives in order to produce a binderless storage phosphor screen on a support with low X-ray absorption, and low "backscattering" even if the storage

- 8 -

phosphor layer is applied by vacuum deposition at fairly high temperatures. Amorphous carbon film supports suitable for use in the present invention are commercially available through, e.g., Tokay Carbon Co, LTD of Tokyo, Japan or Nisshinbo Industries, Inc of Tokyo, Japan, where they are termed "Glass-Like Carbon Film", or "Glassy Carbon". Amorphous carbon is moreover suitable to be applied in the production of binderless phosphor screens by means of chemical vapour deposition in vacuum, as the support on which the phosphor is deposited can be heated up to a temperature of about 10 400°C, thus requiring use of a thermostable support. Therefore, though being a support containing only elements with a low atomic number, a polymeric support is not the most suitable, opposite to more preferred amorphous carbon supports.

- 15 In a phosphor panel or screen according to the present invention, the thickness of the amorphous carbon layer can range from 100 µm up to 3000 µm, a thickness between 500 µm and 2000 µm being preferred as a compromise between flexibility, strength and X-ray absorption. The phosphor screens or panels as described in EP-Application No. 02100764, filed June 28, 2002, provided with a lead foil as an intermediate layer between the said a-C layer support and the phosphor layer are thus highly preferred within the scope of the present invention.
- 25 Otherwise it may be advantageous to provide stimulable phosphor screens with a substrate, characterised in that said substrate has a reflectivity of more than 80% as disclosed in EP-Application No. 02100763, filed June 28, 2002. Said reflectivity is preferably provided by an aluminum layer covering the support or substrate as 30 disclosed therein. Also in US-A-4 618 778 it has also been disclosed to add a reflecting layer between the support and the layer containing the phosphor dispersed in a binder as is, in a particular embodiment of the present invention, applied herein.
- 35 In US-A-4 769 549 and US-A-4 963 751 wherein storage phosphor screens with binderless, vapour deposited phosphor layers are

disclosed, it is suggested that in such screens the compromise between speed and sharpness is so good, that it is not required to include special measures for further increasing the compromise between sharpness and speed, but from the teachings of in EP-
5 Application No. 01000697, filed December 3, 2001, it has advantageously been learned that even with binderless stimulable phosphor screens with vapour deposited phosphors, already showing high speed combined with high sharpness, a better speed/sharpness compromise could be reached when the screen layer arrangement
10 comprises a support covered with a layer absorbing the stimulating light up to more than 30 % and reflecting at least 60 % of the stimulated light. Depending on the needs the balance between reflecting and absorbing properties of the system is optimised: when priority is given to a high speed a reflectance of 80 % will be
15 strived at, whereas, when a higher sharpness is envisaged (as e.g. in mammographic systems) reflection should be lower but an absorption of up to 80 % will be required.

According to the present invention the lead containing layer
20 covering the support absorbs at least 80 % (in mammographic applications) of the stimulating light and reflects at least 80 % (in generally applied radiography) of the stimulated light. In a particular embodiment the said layer is covered with an adjacent thin layer, e.g. an aluminum or another reflecting layer, in order
25 to reach the values set forth above. As a layer of lead has reflecting properties, use can be made thereof as such, in order to further optimise the layer arrangements in the storage phosphor panel, and in order to get an optimised image definition. In the alternative, with respect to reflecting properties, use can be made
30 of a lead foil in combination with a thin reflecting aluminum foil.

As is known in the art of the manufacture of storage screens, wherein storage phosphors are dispersed in a binder, colouring the screen is applied in favour of increasing sharpness. So e.g. in
35 US-A-4 394 581 and US-A-4 491 736 such screens are disclosed. In the present invention however it is understood that although the

- 10 -

support may be coloured, presence of a layer of lead as an intermediate layer between support and phosphor layer makes that any advantageous effect with respect to coloured layers should be expected from coloured phosphor layers and not from coloured supports.

It is clear that storage phosphor panels are not restricted to "binderless storage phosphors" as the "vapour deposited phosphors" further, throughout this text, meant as phosphors produced by any method selected from the group consisting of thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition. This vapour deposition is preferably carried out under conditions as described in EP-A-1 113 458.

Also conventional phosphors as the conventional CsI:Eu phosphor as in Fig. 2 may be used wherein in that panel, in a particular embodiment a layer of lead glass (2') between a conventional phosphor layer (1') with CsI:Eu as conventional phosphor and an electronic detector (CCD, Diode array) as layer (3') is illustrating a panel according to the present invention. Apart for the said conventional phosphors, well-known storage phosphors as e.g. BaFBr-type phosphors known from US-A 5,514,298, are advantageously applied in a panel as set forth in Fig. 1, showing a storage phosphor panel having a lead foil as an intermediate layer between support (3) (PET, Al, Glass, Amorphous Carbon) and phosphor layer (1), coated with a stimulable phosphor (BaFBr:Eu, CsBr:Eu), wherein lead foil (2) is situated as an intermediate layer inbetween phosphor layer (1) and support (3).

Preferred supports for a storage phosphor screen of the present invention are selected from the group consisting of ceramics, glass, polymeric film and amorphous carbon as set forth hereinbefore. Of the polymeric films, especially heat stable polyester films (as e.g. polyethylene terephthalate and polyethylene naphthalate) with a thickness between 100 and 1000 µm are preferred as support in a screen according to the present invention. In order to reach the

desired absorption and reflection properties, the supports, used in screens of the present invention, are treated so that, apart from the desired lead containing layer as a specific layer, no special layers should additionally be coated on the supports in case of 5 vapour deposition of needle-shaped phosphors.

When the support for use in a storage phosphor screen of the present invention is glass, it is preferred to use frit glass made by heating glass particles or fibres at high enough a temperature in order to fuse them together in a manner, sufficiently to form a 10 plate. The surface of such a plate of frit glass is uneven and the profile depends on the diameter of the glass beads used to form the plate of frit glass. The lead containing layer may further depict the unevenness in the support for vapour depositing a phosphor. This is a quite desirable embodiment, because it may help to vapour 15 deposit the phosphor crystals in needle-shaped form if desired.

In a further embodiment a flexible layer of lead or lead oxide is provided on a flexible, polymeric support, with an adhesive layer onto said support and a layer of lead or lead oxide dispersed in a 20 binder, coated over said adhesive layer. These lead or lead oxide layers have, as a particular advantage that they do not absorb moisture and that such a flexible lead or lead oxide layer coated onto a polymeric support has a reduced propensity to produce static electricity during use.

As a barrier layer present on one or both sides of the intermediate lead foil or layer present on the support of the screen or panel of the present invention, a lacquer layer may be provided, wherein any 25 of the well-known lacquers may be used to provide a thin, tough, transparent overcoat for the lead foil screen whereupon the needle-shaped stimulable phosphor may be deposited. The lacquers may be applied as a liquid by any conventional manner and dried to form a tough, smooth overcoat finish to the element. Moreover a fluorosurfactant layer may be applied on top of said lacquer layer.

- 12 -

A polyethylene terephthalate film support coated with an adhesive, whereto a lead foil is applied, is advantageously laminated to this support and allowed to dry to insure good adhesion thereto. As another layer on top of the lead foil layer, a lacquer layer
5 comprising e.g. polymerized polyvinyl chloride may be coated on this adhesive layer and dried. A thin layer of a fluorosurfactant may then be applied over the lacquer layer and the structure dried thoroughly. A flexible, lead layer is thus provided as a substrate of the stimulable phosphor screen layer of the screen or panel
10 according to the present invention.

It was surprising to find that the use of lead or lead oxide on a support layer as set forth hereinbefore would produce such improved results related with image sharpness, due to less scattering of
15 incident X-rays. Furtheron the storage screen or panel of the present invention does not lay burden on the applied system with respect to moisture and curl and other undesirable side-effects like e.g. static charge. The screens not having susceptibility to absorption of moisture and further having antistatic characteristics
20 moreover provide excellent image definition or sharpness.

Lead foils or lead oxide dispersed in a binder are commercially available. A lead foil of differing thicknesses can be applied, but preferred is a lead foil having a thickness of from 25 µm up to 150
25 µm.

The ultimately chosen thickness strongly depends on the application as envisaged and on the energy of the incident X-rays related therewith.

30 A lead foil layer may, besides Pb contain other metals up to a minor extent as e.g. Sn and Sb. This lead foil is then applied to the film support using a conventional adhesive therefor. As a commercially available adhesive e.g. UK 2600 mixed with Zappon® blue and supplied by BASF, Dusseldorf, Germany, may e.g. be used. Other
35 adhesives can also be used as long as they are compatible with the lead layer and as long as they do not interfere with the recording

of an X-ray image. After application of a suitable layer of adhesive to the film support, the lead foil layer is then laminated thereto.

Lead oxide dispersed in a suitable binder and coated in a layer onto the preferred polymeric support may be used as a substituent for a lead foil. Any of the conventional binders as those used for the dispersion of phosphors in layers of intensifying screens may be used herein. Such binders include e.g. polyvinyl butyral, polyvinyl acetate, urethane, polyvinyl alcohol, polyester resins, polymethyl methacrylates and the like. According to the present invention in the storage phosphor screen or panel said binder containing the lead compound is selected from the group consisting of polyvinyl butyral, polyvinyl acetate, urethane, polyvinyl alcohol, polyester resins and polymethyl methacrylates. Conventionally, the binders are mixed with a suitable solvent and conventional wetting agents as dispersion aids of the lead oxide therein. The level of binder present should be kept low versus the dispersed lead oxide in order to provide a thin substrate coated with lead.

In one embodiment a support provided with an elastomeric layer thereupon, having a metal-containing filler therein, may be used.

Apart from a polymeric support, an aluminum layer may be used coated with a layer of poly(vinylidene fluoride-hexafluoro-propylene) copolymer having a metal-containing filler, such as lead oxide, dispersed therein.

As an alternative for the lead oxide a lead salt may be used, said salt being selected from the group consisting of lead carbonate, lead acetate, lead iodide, lead chloride, lead fluoride, lead sulfide, lead sulfate and lead nitrate.

Lead-based paint may be used and applied by the well known coating techniques, as e.g. silk screen printing, in order to provide an embossed layer, whereupon the needle-shaped phosphor may be deposited.

- 14 -

Substates such as glass panes or polymeric supports, all of them suitably cleaned, may, in the alternative, be subjected to magnetron sputtering procedures from a series of target cathodes, wherein the amount of each sputter coated material may be controlled by varying the number of cathodes beneath which the supports are passed during the coating operation. So directly upon the glass surface or polymeric support may be deposited a layer of lead oxide from a lead cathode operating in an oxygen-argon environment.

In the particular application related with mammography wherein exposure with soft X-rays occurs, lead oxide layers may so be deposited to an approximate thickness of about 50 Angstroms. For all other exposures, more rich in energy, it is clear that a higher thickness of the absorbing layer is more preferred.

Details about magnetron sputtering procedures can e.g. be found in -K. Wasa and S. Hayakawa, "Efficient Sputtering in a Cold-Cathode Discharge in Magnetron Geometry", Proc. of the IEEE, 55, 2179 (Dec. 1967).

-S. D. Gill and E. Kay, "Efficient Low Pressure Sputtering in a Large Inverted Magnetron Suitable for Film Synthesis", Review of Scientific Instruments, 36:277-282 (Mar. 1965).

-James R. Mullaly, "A Crossed-Field Discharge Device for High Rate Sputtering", RFP-1310, The Dow Chemical Company, Nov. 13, 1969, U.S. Atomic Energy Commission Contract AT(29-1)-1106.

-I. G. Kesaev and V. V. Pashkova, "The Electro Magnetic Anchoring of the Cathode Spot", Sov. Phys. Tech. Phys., vol. 3, pp. 254-264 (1959) [English Translation of Zh. Tekh. Fiz., vol. 29, pp. 287-298 (1959)].

-K. Wasa and S. Hayakawa, "Low Pressure Sputtering System of the Magnetron Type", Rev. Sci. Inst., vol. 40(5), pp. 693-697 (1969).

-A. M. Dorodnov, "Some Applications of Plasma Accelerators in Technology", pp. 330-365 in Fisika i Primenenie Plasmennich Uskoritelej (A. I. Morosov, Ed.) Nauka i Tehnike, Minsk (1974).

-J. R. Mullaly, "Crossed Field Discharge Device for High Rate

Sputtering," Research/Development, vol. 22, pp. 40; 42, and 44 (Feb. 1971).

Sol-gel reactions have recently been used in order to prepare
5 inorganic-organic composite materials. This general reaction, making
use of hydrolysis and polycondensation of a metal alkoxide species,
is preferably applied in order to provide a layer having lead oxide
in the layer arrangement of the screen or panel of the present
invention. According to the present invention, in a particular
10 embodiment said binder containing the lead compound in the storage
screen or panel of the present invention, is a matrix of a
polycondensation product of a metal alkoxide species. Said
reactions take place under the influence of a suitable catalyst as
e.g. an acid, and a network is formed in the process. Further
15 according to a preferred embodiment of the present invention said
binder containing the lead compound is a matrix of an inorganic
network of alkoxymetal substituted organic polymers or copolymers
matrix.

20 During the build-up of this inorganic network alkoxymetal
substituted organic polymers or copolymers are also present in the
reaction medium and also undergo the same polycondensation reaction
as the hydrolyzed metal alkoxides and are also incorporated in the
network. In a further embodiment according to the present invention
25 said binder containing the lead compound is a matrix of an inorganic
network of alkoxymetal substituted organic polymers or copolymers
matrix.

Particular types of inorganic-organic composite materials are named
30 ORMOCERS (ORganically MOdified CÉramics), ORMOSILS (Organically
MOdified SILicates) or CERAMERS. Scientific literature on inorganic-
organic composite materials includes:

"The synthesis, structure and property behaviour of inorganic-
organic hybrid network materials prepared by the sol-gel process",
35 Wilkes et al., Proceedings of MRS Meeting, Boston Mass., November
1989;

- 16 -

"Sol-gel processes II: investigation and application", H. Reuter,
Advanced Materials, 3 (1991) No 11, p. 568;

"New inorganic-organic hybrid materials through the sol-gel
approach", Wilkes et al., Chemistry of Materials, 1996, part VIII,
5 p. 1667-1681.

"Hybrid inorganic-organic materials by sol-gel processing of
organofunctional metal alkoxides", Schubert et al., Chem. Mater.
(1995), 7, p. 2010-2027.

10 In one embodiment the screen or panel according to the present invention is thus provided with an intermediate layer wherein said lead compound is an oxide or a hydroxide of lead metal, dispersed in a binder. In a preferred embodiment the phosphor screen or panel according to the present invention has a binder containing the lead compound in a layer comprising a cross-linked polymeric matrix, wherein said matrix is derived from a cross-linking agent selected from the group consisting of dialkoxy silanes, trialkoxy silanes, tetraalkoxy silanes, titanates, zirconates and aluminates; and a colloid of silica, and wherein said matrix comprises a colloid of an oxide or a hydroxide of lead metal. So in the alternative the support may be coated with a hydrophilic layer comprising a cross-linked polymeric matrix, wherein said matrix is derived from a cross-linking agent selected from the group consisting of dialkoxy silanes, trialkoxy silanes, tetraalkoxy silanes or, in the 20 alternative, titanates, zirconates and aluminates; and a colloid of silica, and wherein said matrix comprises a colloid of an oxide or a hydroxide of lead metal. The amount of silica in the layer preferably is in the range from 1 up to 50 times the amount of cross-linking agent. In the cross-linked polymeric matrix use is 25 preferably made from N-trimethoxy-N,N,N-trimethyl ammonium chloride, 3-aminopropyltrimethoxysilane; a mixture of dimethyl dimethoxysilane and methyl trimethoxysilane sold as Z-6070 by the Dow Corning Company and glycidoxypropyltrimethoxysilane, without however being limited thereto.

35

A binderless phosphor screen according to the present invention

can be prepared by vacuum deposition of the phosphor crystals on the substrate as well as by combining (mixing) the ingredients for the phosphor (phosphor precursors) and then evaporating this mixture in order to have the phosphor formed in situ during evaporation.

5

According to the present invention it is further preferred to provide a binderless stimulable phosphor screen on a polymeric film covered with a lead layer as a substrate in an intermediate layer, wherein said intermediate layer has a surface that has been subjected to embossing for forming a fine concavo-convex pattern. The phosphor in a binderless phosphor screen according to the present invention can be any stimulable phosphor known in the art. Preferably the storage phosphor used in binderless phosphor screens phosphor is a binderless phosphor, having needle-shaped crystals and in an even more preferred embodiment said needle-shaped phosphor crystals are crystals of an alkali metal phosphor.

Very suitable phosphors are, e.g., phosphors according to the formula I :



wherein:

M^{1+} is at least one member selected from the group consisting of Li, Na, K, Cs and Rb,

25 M^{2+} is at least one member selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Pb and Ni,

M^{3+} is at least one member selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Bi, In and Ga,

30 Z is at least one member selected from the group Ga^{1+} , Ge^{2+} , Sn^{2+} , Sb^{3+} and As^{3+} , X, X' and X'' can be the same or different and each represents a halogen atom selected from the group consisting of F, Br, Cl, I and $0 \leq a \leq 1$, $0 \leq b \leq 1$ and $0 < c \leq 0.2$. Such phosphors have been disclosed in, e.g., US-A-5 736 069.

- 18 -

Highly preferred phosphors for use in a binderless phosphor screen of the present invention are CsX:Eu stimulable phosphors, wherein X represents a halide selected from the group consisting of 5 Br and Cl prepared by a method comprising the steps of :

- mixing said CsX with an amount of between 10^{-3} and 5 mole % of a Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being a member selected from the group consisting of F, Cl, Br and I;
- 10 - firing said mixture at a temperature above 450°C ;
- cooling said mixture and
- recovering the CsX:Eu phosphor.

Most preferably a CsBr:Eu stimulable phosphor is used, wherein 15 said phosphor is prepared by the method comprising the steps of :

- mixing said CsX with an amount of between 10^{-3} and 5 mole % of a Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being a member selected from the group consisting of F, Cl, Br and I;
- 20 - firing said mixture at a temperature above 450°C ;
- cooling said mixture and
- recovering the CsX:Eu phosphor.

The binderless screen can be prepared by bringing the finished 25 phosphor on the support by any method selected from the group consisting of thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition. It is also possible to bring the alkali metal halide and the dopant together and depositing them both on the support in such a way that the alkali metal phosphor is doped during 30 manufacturing the screen.

Thus the present invention encompasses a method for manufacturing a phosphor screen containing a CsX:Eu stimulable

phosphor, wherein X represents a halide selected from the group consisting of Br and Cl comprising the steps of :

- bringing multiple containers of said CsX and a Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being a halide selected from the group consisting of F, Cl, Br and I in condition for vapour deposition and
- depositing, by a method selected from the group consisting of thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition, both said CsX and said Europium compound on a substrate in such a ratio that on said substrate a CsX phosphor, doped with an amount between 10^{-3} and 5 mole % of Europium, is formed.

The deposition can proceed from a single container containing a mixture of the starting compounds in the desired proportions. Thus the method further encompasses a method for manufacturing a phosphor screen containing a CsX:Eu stimulable phosphor, wherein X represents a halide selected from the group consisting of Br and Cl comprising the steps of :

- mixing said CsX with an amount between 10^{-3} and 5 mole % of a Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being a halide selected from the group consisting of F, Cl, Br and I;
 - bringing said mixture in condition for vapour deposition and
 - depositing said mixture on a substrate by a method selected from the group consisting of physical vapour deposition, thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition.
- Apart for applications in "needle-shaped phosphors", and more particularly, in applications with columnar CsBr:Eu needles, screens or panels coated with "powdered phosphors" in general radiographic diagnosis are particularly envisaged. Even more particularly is its application in mammography for the reason, already set forth hereinbefore, the more as the phosphor layer should be very thin (in

- 20 -

the range of "about 150 µm) so that X-rays are easily passing through the phosphor layer, thereby generating much more backscattering radiation in the layers underlying the phosphor layer.

5 Further apart for applications in digital radiography, "direct radiography" is also envisaged as in such an application, wherein an electronic detector is in direct contact with an electronic detector, providing direct processing of the signals obtained as already illustrated in Fig. 2. In an analogous way it is understood
10 that sharpness is not only determined for such a direct radiographic system by the thickness of the phosphor layer, but also by the scattering properties of the underlying diode array of CCD's. An additional requirement is presence of a transparent foil, which cannot form a problem if e.g. use is made of lead glass: application
15 of a thin layer (see layer (2') in Fig. 2) thereof between phosphor layer and electronic detector will improve sharpness to a remarkable extent.

The invention moreover includes a storage phosphor panel comprising
20 the steps of :

- providing a suitable support (e.g. an amorphous carbon film) coated with an intermediate lead containing sheet or foil as a substrate material for the phosphor plate or panel,

25 - vacuum depositing a storage phosphor layer onto said substrate material and

- optionally laminating a polymeric film on the side of the substrate material not covered by said phosphor.

The invention further includes a method for producing a storage
30 phosphor panel comprising the steps of :

- providing a suitable support (e.g. an amorphous carbon film) coated with an intermediate lead sheet or foil as a substrate material for the phosphor plate or panel,

35 - applying a specularly reflecting layer thereupon,

- further vacuum depositing a storage phosphor layer on said reflecting layer, and

- optionally laminating a polymeric film on the side of the reflecting layer not covered by said phosphor.

The invention further includes a method for producing a storage phosphor panel comprising the steps of :

- providing a suitable support (e.g. an amorphous carbon film) coated with an intermediate lead sheet or foil as a substrate material for the phosphor plate or panel,
- applying a specularly reflecting layer thereupon,
- chemical vacuum depositing a moisture repellent layer (preferably a parylene layer) on top of said specularly reflecting layer,
- further vacuum depositing a storage phosphor layer on said reflecting layer, optionally polishing said phosphor layer, and, furtheron, optionally,
- laminating a polymeric film on the side of the amorphous carbon film not covered by said phosphor.

The screen or panel of the present invention moreover may include on top of the phosphor layer any protective layer known in the art.

Especially suitable however for use are those protective layers disclosed in EP-Applications Nos. 02100297, filed March 26, 2002; and 01000694 and 01000695, both filed December 3, 2001.

In order to provide an image storage panel having high surface durability, i.a. avoiding damaging of the surface by stain and abrasion after multiple use, further in favour of ease of manipulation, excellent image quality (improved sharpness) without screen structure noise increase the radiation image storage panel comprises a protective coating characterized in that, besides a binder, the said protective coating comprises a white pigment having a refractive index of more than 1.6, more preferably a refractive index of more than 2.0, and even more defined, titanium dioxide, which is present in the said binder, optionally further comprising a urethane acrylate, and wherein said protective coating has a surface roughness (R_z) between 2 μm and 10 μm as disclosed in EP-Application No. 01 000 711, filed December 5, 2001.

- 22 -

In the alternative the protective layer is composed of a polymeric compound selected from the group consisting of vinyl resins comprising moieties derived from esters of acrylic acid and vinyl resins comprising moieties derived from esters of methacrylic acid 5 and, even more preferably, a thermoplastic rubber as disclosed in EP-Application No. 02 100 235, filed March 8, 2002. In favour of sharpness the polymer further comprises at least one colourant, and more preferably, a colourant having same absorption characteristics with respect to stimulating radiation as the colourant deposited by 10 chemical vapour deposition as described above.

As an outermost layer, a parylene layer is highly desired as moisture proof layer as has e.g. been described in EP-Application No. 01000401.8, filed August 23, 2001. In still another embodiment according to the present invention a binderless photostimulable 15 phosphor screen is provided, overcoated with a vacuum deposited protective layer of poly(p-xylylene) (=parylene), poly(p-2-chloro-xylylene), poly(p-2,6-dichloroxylylene) and fluoro substituted poly(p-xylylene), MgF₂, or a combination thereof. As chemical vapour deposition is a technique that can be applied when making use 20 of those components, the said technique is advantageously applied in this case. "Parylene" thereby particularly provides excellent moisture resistance, whereas MgF₂ offers excellent anti-reflecting properties.

25 The screen or the panel of the present invention can also have reinforced edges as described in, e.g., US-A-5 334 842 and US-A-5 340 661.

The surface of the phosphor layer (1) in a panel or screen of 30 the present invention can be made smaller than the surface of the support (2) so that the phosphor layer does not reach the edges of the support. Such a screen has been disclosed in, e.g., EP-Application No. 02100297, filed March 26, 2002.

The present invention moreover includes a method for exposing an object to X-rays comprising the steps of :

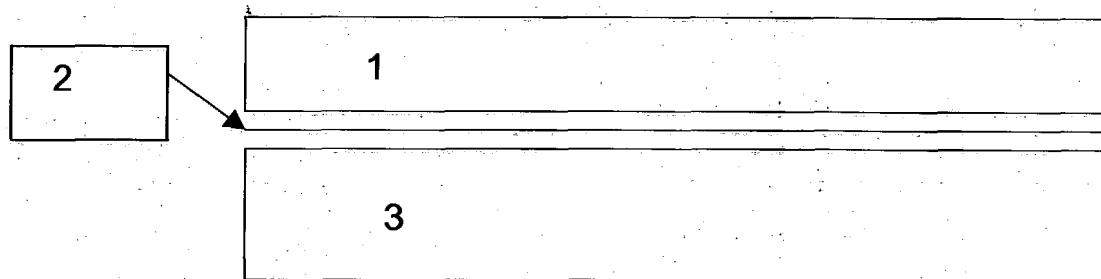
- providing an X-ray machine including an X-ray tube equipped for emitting X-rays with an energy lower than or equal to 70 keV and a phototimer coupled to said X-ray tube for switching said tube on and off in accordance with an X-ray dose reaching said phototimer,
- placing an object between said X-ray tube and said phototimer
- placing a binderless storage phosphor panel or screen according to the present invention between said object and said phototimer and
- activating said X-ray tube for exposing said object, said cassette and said phototimer until said phototimer switches said X-ray tube off.

Having described in detail preferred embodiments, it is clear that those embodiments should not be limited thereto.

[CLAIMS]

1. A stimulable phosphor screen or panel comprising a phosphor layer and a support characterised in that an intermediate layer of lead or a layer comprising a lead compound is present between said support and said phosphor layer.
2. A phosphor screen or panel according to claim 1, wherein said lead compound is an oxide or a hydroxide of lead metal, dispersed in a binder.
3. A phosphor screen or panel according to claim 2, wherein said binder containing the lead compound is selected from the group consisting of polyvinyl butyral, polyvinyl acetate, urethane, polyvinyl alcohol, polyester resins and polymethyl methacrylates.
4. A phosphor screen or panel according to claim 2, wherein said binder containing the lead compound is a matrix of a polycondensation product of a metal alkoxide species.
5. A phosphor screen or panel according to claim 4, wherein said binder containing the lead compound is a matrix of an inorganic network of alkoxymetal substituted organic polymers or copolymers matrix.
6. A phosphor screen or panel according to claim 5, wherein said binder containing the lead compound is in a layer comprising a cross-linked polymeric matrix, wherein said matrix is derived from a cross-linking agent selected from the group consisting of dialkoxy silanes, trialkoxy silanes, tetraalkoxy silanes, titanates, zirconates and aluminates; and a colloid of silica, and wherein said matrix comprises a colloid of an oxide or a hydroxide of lead metal.

7. A phosphor screen or panel according to any one of the claims 1 to 6, wherein said support is selected from the group consisting of ceramics, glass, amorphous carbon and polymeric films.
8. A phosphor screen or panel according to any one of the claims 1 to 7, wherein said intermediate layer has a surface that has been subjected to embossing for forming a fine concavo-convex pattern.
9. A phosphor screen or panel according to any of claims 1 to 8, wherein said phosphor is a binderless phosphor, having needle-shaped crystals.
10. A binderless stimulable phosphor screen or panel according to claim 9, wherein said needle-shaped phosphor crystals are crystals of an alkali metal phosphor.
11. A binderless stimulable phosphor screen according to claim 10, wherein said alkali metal phosphor is a CsX:Eu stimulable phosphor, wherein X represents a halide selected from the group consisting of Br and Cl, said phosphor being prepared by a method comprising the steps of :
 - mixing said CsX with an amount between 10^{-3} and 5 mole % of a Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being a member selected from the group consisting of F, Cl, Br and I,
 - firing said mixture at a temperature above 450°C
 - cooling said mixture and
 - recovering the CsX:Eu phosphor.

Fig. 1**Fig. 2**